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# Design of I<sub>2</sub>-II-IV-VI<sub>4</sub> Semiconductors through Element-substitution: the Thermodynamic Stability Limit and Chemical Trend

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## ABSTRACT:

Through element substitution in Cu<sub>2</sub>ZnSnS<sub>4</sub>, a class of I<sub>2</sub>-II-IV-VI<sub>4</sub> semiconductors can be designed as novel functional materials. Using the first-principles calculations, we show that this element-substitution design is thermodynamically limited, i.e., although I<sub>2</sub>-II-IV-VI<sub>4</sub> with I=Cu, Ag, II=Zn, Cd, Hg, IV=Si, Ge, Sn and VI=S, Se, Te are stable quaternary compounds, those with II=Mg, Ca, Sr, Ba, IV=Ti, Zr, Hf, and VI=O are unstable against the phase-separation into the competing binary and ternary compounds. Three main phase-separation pathways are revealed. In general, we show that if the secondary II-VI or I<sub>2</sub>-IV-VI<sub>3</sub> phases prefer to have non-tetrahedral structures, then the I<sub>2</sub>-II-IV-VI<sub>4</sub> semiconductors tend to phase separate. This finding can be used as a guideline for future design of new quaternary semiconductors.

## I. INTRODUCTION

Because all component elements are earth-abundant and environment-friendly, the quaternary semiconductors Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe) and their alloys with band gaps between 1.0-1.5 eV have been intensively studied as low-cost and sustainable solar cell absorber materials during the last five years<sup>1-5</sup>. Through substituting Cu by other group I (+1 valence) cations, Zn by group II (+2 valence) cations, Sn by group IV (+4 valence) cations, and S or Se by group VI anions (-2 valence), a class of I<sub>2</sub>-II-IV-VI<sub>4</sub> quaternary semiconductors, such as Cu<sub>2</sub>ZnGeS<sub>4</sub><sup>4, 6</sup>, Ag<sub>2</sub>CdSnSe<sub>4</sub><sup>7</sup> and Cu<sub>2</sub>CdGeSe<sub>4</sub><sup>8</sup>, can be designed. These quaternary semiconductors have tetrahedrally coordinated crystal structures (derived from zincblende or wurtzite structure) and electronic structure (s-p band gap) similar to the binary II-VI semiconductors (ZnS, CdTe)<sup>9</sup>, but their properties are much more diverse given the increased number of elements, so they may have wide applications in electronic, optoelectronic, photovoltaics, or photocatalytic applications<sup>10-13</sup>.

This element-substitution design had been proposed as early as 1960s<sup>14, 15</sup>, and a

series of quaternary semiconductors had been synthesized, e.g.,  $I_2-II-IV-VI_4$  with  $I=Cu$ ,  $Ag$ ,  $II=Zn$ ,  $Cd$ ,  $IV=Si$ ,  $Ge$ ,  $Sn$ ,  $Pb$ , and  $VI=S$ ,  $Se$ , as listed in the semiconductor handbooks<sup>16</sup>. Recently, new design goes beyond these conventional elements, e.g.,  $Cu_2ZnTiS_4$ ,  $Cu_2MgSiS_4$ , and  $Cu_2MgGeS_4$  were proposed theoretically as new functional materials<sup>17, 18</sup>, and  $Cu_2MgGeS_4$  had even been synthesized, which shows X-ray diffraction pattern in good agreement with that of the theoretically proposed structure<sup>17</sup>. The synthesis of some other  $I_2-II-IV-VI_4$  compounds had also been reported. For example,  $Cu_2ZnSn(S,O)_4$  (alloy of  $Cu_2ZnSnS_4$  and  $Cu_2ZnSnO_4$ ) was synthesized using chemical vapor deposition method by Washio et al.<sup>19</sup>, and  $Cu_2BaSnS_4$ ,  $Ag_2BaSnS_4$  and  $Cu_2SrSnS_4$  were synthesized from a mixture of three binary sulfides by Teske et al.<sup>20, 21</sup> Since there are many elements with +1, +2, +4 and -2 valences, e.g.,  $II=Mg$ ,  $Ca$ ,  $Sr$ ,  $Ba$  (group IIA),  $IV=Ti$ ,  $Zr$ ,  $Hf$  (group IVB) and  $VI=O$ ,  $Te$ , their combination can lead to a large number of potential  $I_2-II-IV-VI_4$  compounds.

As more and more  $I_2-II-IV-VI_4$  semiconductors are designed or reported, one fundamental issue is whether the proposed  $I_2-II-IV-VI_4$  semiconductors are thermodynamically stable. Currently, this question is not yet systematically addressed. Furthermore, the possible factors or mechanism that may cause the instability are also unclear. The answer to these questions is important for theoretical design and experimental synthesis of novel and stable  $I_2-II-IV-VI_4$  compounds.

In this work, a series of  $I_2-II-IV-VI_4$  semiconductors are studied through the first-principles calculations. Based on the analysis of the calculated results, the thermodynamic limiting mechanism to the stability of  $I_2-II-IV-VI_4$  semiconductors is revealed. The results show that although the substitution of  $II$  by  $Zn$ ,  $Cd$ ,  $Hg$ ,  $IV$  by  $Si$ ,  $Ge$ ,  $Sn$  and  $VI$  by  $S$ ,  $Se$ ,  $Te$  can lead to stable quaternary compound semiconductors, the substitution of  $II$  by  $Mg$ ,  $Ca$ ,  $Sr$ ,  $Ba$ ,  $IV$  by  $Ti$ ,  $Zr$ ,  $Hf$ , and  $VI$  by  $O$  has limited thermodynamic stability because the phase-separated competing binary and ternary compounds are more stable in different local environment than that in the tetrahedral environment of the  $I_2-II-IV-VI_4$  compounds. When an  $I_2-II-IV-VI_4$  compound is unstable, the corresponding elements can only be incorporated into a stable  $I_2-II-IV-VI_4$  with low concentration, thus their contribution to tuning the material properties is limited.

## II. COMPUTATIONAL DETAILS

The crystal and electronic structure calculations are performed based on the density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) code<sup>22</sup>. For the exchange correlation potential, we use the generalized gradient approximation (GGA) of Perdew and Wang<sup>23</sup>. The projector augmented-wave pseudopotentials<sup>24</sup> and the plane-wave basis functions are used with an energy cutoff of 400 eV in the study of all sulfide, selenide and telluride compounds and an energy cutoff of 500 eV in the study of oxide compounds. For the Brillouin zone integration,

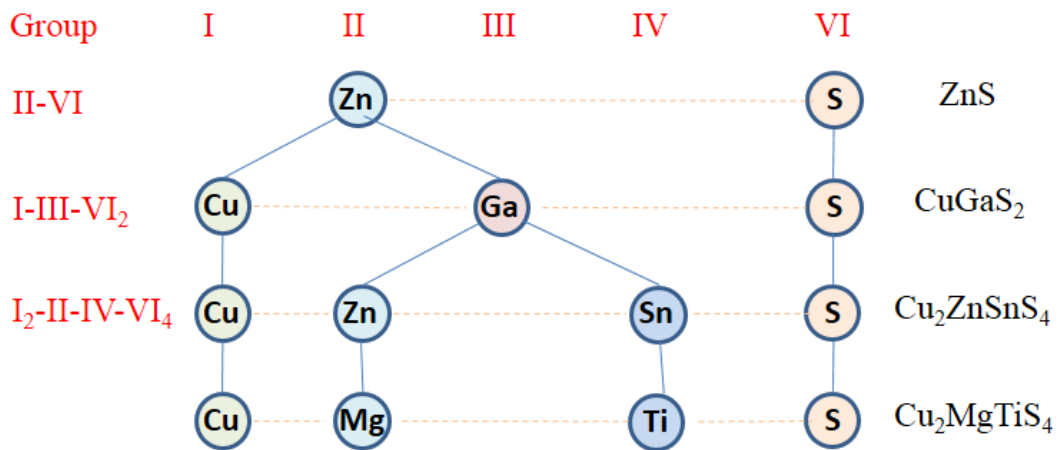
an  $8 \times 8 \times 4$  Monkhorst–Pack or equivalent k-point meshes are used. All lattice vectors and atomic positions are fully relaxed by minimizing the quantum-mechanical stresses and forces. The total energies used for assessing the heats of formation are converged to within 0.001 eV / atom. No temperature dependent effects are considered.

### III. RESULTS AND DISCUSSION

#### 3.1. Element-substitution Design of $I_2-II-IV-VI_4$

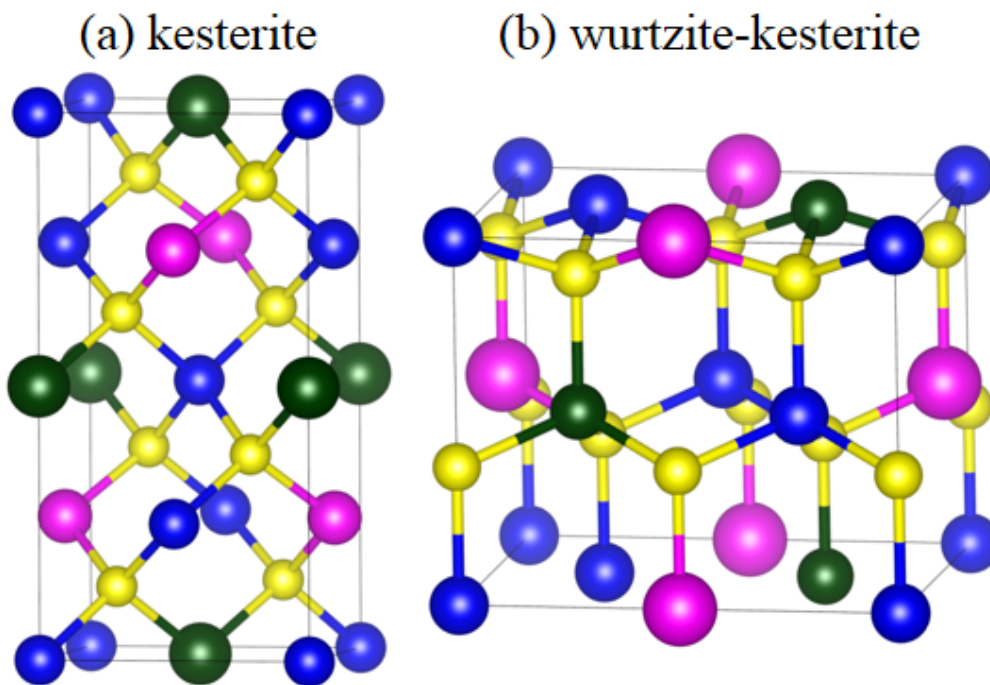
The quaternary  $I_2-II-IV-VI_4$  semiconductors can be taken as derived from binary II-VI semiconductors<sup>25</sup>, e.g.,  $Cu_2ZnSnS_4$  from  $ZnS$ , as shown schematically in Figure 1. In zincblende  $ZnS$ , the  $S^{2-}$  anion is tetrahedrally bonded with four  $Zn^{2+}$  cations. If the four  $Zn^{2+}$  are replaced by two  $Cu^+$  and two  $Ga^{3+}$  cations, the ternary  $CuGaS_2$  semiconductor can be derived, and if the two  $Ga^{3+}$  cations are further replaced by one  $Zn^{2+}$  and one  $Sn^{4+}$  cation, quaternary  $Cu_2ZnSnS_4$  can be derived. The elements of  $Cu_2ZnSnS_4$  can also be replaced by other isovalent elements, such as Zn by Mg, Sn by Ti, and S by Se, then a series of  $I_2-II-IV-VI_4$  semiconductors (such as  $Cu_2MgTiS_4$ ) can be derived, as shown in Fig. 1. In this study, we focus on the following series of component elements:

- I: Cu
- II: Zn, Cd, Hg; Mg, Ca, Sr
- IV: Si, Ge, Sn, Pb; Ti, Zr, Hf
- VI: O, S, Se, Te



**Figure 1.** A schematic plot of the derivation of  $I_2-II-IV-VI_4$  semiconductors from binary II-VI and ternary I-III-VI<sub>2</sub> parent compounds.

During the replacement of the component elements, the local charge around each anion always satisfies the octet rule, so the tetrahedrally-coordinated lattice framework of zincblende or wurtzite is kept when it mutates into quaternary structures, despite they have different symmetries depending on the ordering of the cations<sup>25</sup>. Among these quaternary crystal structures, five fundamental structures have been found with the smallest primitive cells and the lowest energy<sup>25, 26</sup>, including kesterite, stannite, primitive-mixed CuAu (PMCA), wurtzite-kesterite, and wurtzite-stannite. Two of those structures are shown in Figure 2. Their total energy difference is usually less than 0.01 eV/atom, so their differences in the compound formation energies are small<sup>24, 25</sup>. Therefore, in our following study, we will use only the representative kesterite structure [Fig. 2(a)] to study the phase stability.



**Figure 2.** The unit cells of (a) zincblende-derived kesterite, (b) wurtzite-derived wurtzite-kesterite  $I_2-II-IV-VI_4$  crystal structures. Blue, purple, green and yellow balls show the I, II, IV, and VI atoms, respectively.

### 3.2. Thermodynamic Stability Limit

Although the charge-neutrality condition around each anion is satisfied in the element-substitution design of  $I_2-II-IV-VI_4$  semiconductors, whether they can be synthesized under equilibrium conditions (thermodynamically stable) is a question. The formation of the quaternary compounds is limited, since these component elements can also form other elemental, binary and ternary phases, which are competing with the quaternary phases.<sup>5, 27, 28</sup> To study the competition quantitatively,

we use the chemical potentials of the component elements to describe the richness of these elements in the synthesis environment. If the  $I_2-II-IV-VI_4$  is stable, the chemical potential of the component elements under the equilibrium condition should satisfy,

$$2\mu_I + \mu_{II} + \mu_{IV} + 4\mu_{VI} = \Delta H_f(I_2 - II - IV - VI_4), \quad (1)$$

where  $\Delta H_f(I_2 - II - IV - VI_4)$  is the calculated formation energy of  $I_2-II-IV-VI_4$ , i.e., the energy change of the reaction  $2I+II+IV+4VI \rightarrow I_2-II-IV-VI_4$ , and  $\mu_I$ ,  $\mu_{II}$ ,  $\mu_{IV}$  and  $\mu_{VI}$  are the chemical potentials of the group I, II, IV and VI elements, which are referenced to their respective most stable elemental phases.  $\mu_I=0$ ,  $\mu_{II}=0$ ,  $\mu_{IV}=0$ , and  $\mu_{VI}=0$  mean these elements are so rich that their pure elemental phases can start to form.

To avoid the precipitation of these elemental phases, it is required that  $\mu_I < 0$  and similarly  $\mu_{II} < 0$ ,  $\mu_{IV} < 0$ ,  $\mu_{VI} < 0$ . On the other hand, to avoid the formation of secondary phases such as binary I-VI (e.g., CuS),  $I_2$ -VI ( $Cu_2S$ ), II-VI (ZnS), IV-VI (SnS), IV- $VI_2$  ( $SnS_2$ ) and ternary  $I_2$ -IV- $VI_3$  ( $Cu_2SnS_3$ ), as well as any phases that deviate from the stoichiometry (2:1:1:4) of the  $I_2-II-IV-VI_4$  compound, the following conditions must be satisfied too,

$$\mu_I + \mu_{VI} < \Delta H_f(I - VI) \quad (\text{e.g., } \mu_{Cu} + \mu_S < \Delta H_f(CuS)) \quad (2a)$$

$$2\mu_I + \mu_{VI} < \Delta H_f(I_2 - VI) \quad (\text{e.g., } 2\mu_{Cu} + \mu_S < \Delta H_f(Cu_2S)) \quad (2b)$$

$$\mu_{II} + \mu_{VI} < \Delta H_f(II - VI) \quad (\text{e.g., } \mu_{Zn} + \mu_S < \Delta H_f(ZnS)) \quad (2c)$$

$$\mu_{IV} + \mu_{VI} < \Delta H_f(IV - VI) \quad (\text{e.g., } \mu_{Sn} + \mu_S < \Delta H_f(SnS)) \quad (2d)$$

$$\mu_{IV} + 2\mu_{VI} < \Delta H_f(IV - VI_2) \quad (\text{e.g., } \mu_{Sn} + 2\mu_S < \Delta H_f(SnS_2)) \quad (2e)$$

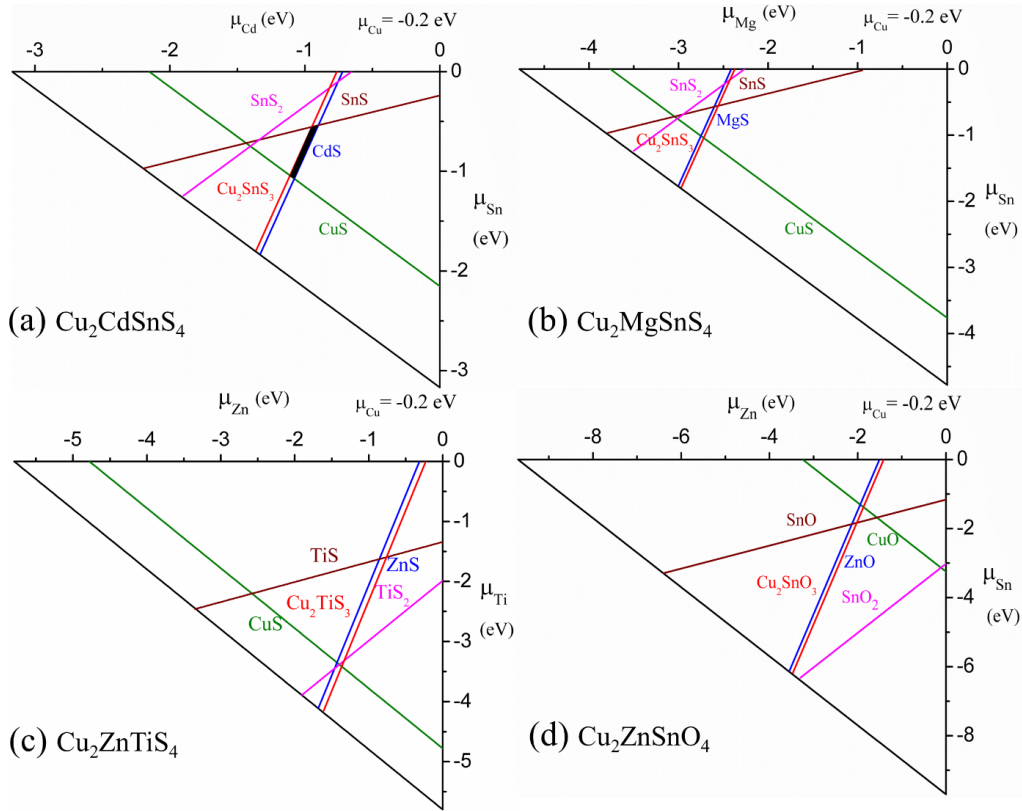
$$2\mu_I + \mu_{IV} + 3\mu_{VI} < \Delta H_f(I_2 - IV - VI_3) \\ (\text{e.g., } 2\mu_{Cu} + \mu_{Sn} + 3\mu_S < \Delta H_f(Cu_2SnS_3)). \quad (2f)$$

Only when all of these conditions are satisfied, the pure  $I_2-II-IV-VI_4$  phase can be stable thermodynamically. These constraints limit the values of  $\mu_I$ ,  $\mu_{II}$ ,  $\mu_{IV}$ ,  $\mu_{VI}$ . Considering Eq. (1), only three of the four chemical potentials are variables, and the other one can be determined, e.g.,  $\mu_{VI}$  can be determined if we take  $\mu_I$ ,  $\mu_{II}$ ,  $\mu_{IV}$  as variables. Under the established constraints, the range of the three variables is bound in a polyhedron in the three-dimensional  $(\mu_I, \mu_{II}, \mu_{IV})$  space<sup>27</sup>, which defines the chemical potential range that stabilizes the  $I_2-II-IV-VI_4$  compounds. In Fig. 3, we plot the slices of the polyhedron in  $\mu_{Cu} = -0.2$  eV plane for four representative  $I_2-II-IV-VI_4$  compounds,  $Cu_2CdSnS_4$ ,  $Cu_2MgSnS_4$ ,  $Cu_2ZnTiS_4$ , and  $Cu_2CdSnO_4$ .

### 3.2.1. Stability of $Cu_2-II-SnS_4$ (II=Zn, Cd, Hg, and Mg, Ca, Sr, Ba)

In Fig. 3(a), the black region shows the chemical potential range that stabilizes  $Cu_2CdSnS_4$ . Six competing secondary compounds, i.e., binary  $Cu_2S$ , CuS, CdS, SnS,

SnS<sub>2</sub> and ternary Cu<sub>2</sub>SnS<sub>3</sub> are considered, and their limit to the stable region is shown by the boundary lines with the same color as their labels. When the chemical potential crosses the line and goes beyond the black region, the corresponding secondary compounds can form, and thus the quaternary phase Cu<sub>2</sub>CdSnS<sub>4</sub> becomes unstable. Besides the  $\mu_{Cu}=-0.2$  eV plane, we also studied the limit to the stable region in other planes with different  $\mu_{Cu}$ , which shows that single-phase Cu<sub>2</sub>CdSnS<sub>4</sub> can be stabilized in a narrow chemical potential region, so it can be synthesized and is thermodynamically stable, which is consistent with the experimental observation that Cu<sub>2</sub>CdSnS<sub>4</sub> had been synthesized by many groups<sup>29-31</sup>.



**Figure. 3.** The limit to the chemical potential regions that stabilize single-phase I<sub>2</sub>-II-IV-VI<sub>4</sub>. Here the limit is imposed by a series of competing compounds, and the plot is in the  $\mu_{Cu}=-0.2$  eV plane. The plot in other planes are also considered, but not shown here.

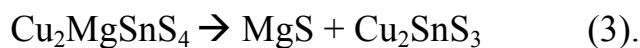
Besides Cu<sub>2</sub>CdSnS<sub>4</sub>, we also calculate the stable region for other Cu<sub>2</sub>-II-SnS<sub>4</sub> compounds with II=Zn, Hg, and they all have a narrow stable region in the chemical potential space, which is also consistent with the widely reported experimental synthesis<sup>32-36</sup>. The stable regions for all the three compounds are narrow, indicating that the composition control is very important for synthesizing these single-phase materials. The most stringent constraints come from CdS and Cu<sub>2</sub>SnS<sub>3</sub>, i.e., when Cd is relatively poor (left side of the black region) in the synthesis environment, Cu<sub>2</sub>SnS<sub>3</sub>

will coexist in the samples, while when Cd is relatively rich (right side of the black region), CdS will coexist. This highlights the necessity to detect these secondary phases in the synthesized samples before the characterization of their properties, otherwise the properties may not be intrinsic to the quaternary  $I_2-II-IV-VI_4$ .

**TABLE I:** The calculated energy change  $\Delta E$  (in eV) of different phase-separation reactions of  $Cu_2-II-SnS_4$  ( $II=Zn, Cd, Hg$ , and  $Mg, Ca, Sr, Ba$ ). If the compound has been synthesized, the references are listed in the Ref. column.

| Compound                        | Phase Separation  | $\Delta E$ | Ref.          | Compound                        | Phase Separation  | $\Delta E$ | Ref. |
|---------------------------------|-------------------|------------|---------------|---------------------------------|-------------------|------------|------|
| <b><math>Cu_2ZnSnS_4</math></b> | $Cu_2S+ZnS+SnS_2$ | 0.56       | <sup>37</sup> | <b><math>Cu_2MgSnS_4</math></b> | $Cu_2S+MgS+SnS_2$ | 0.47       | -    |
|                                 | $2CuS+ZnS+SnS$    | 0.40       | <sup>33</sup> |                                 | $2CuS+MgS+SnS$    | 0.31       |      |
|                                 | $Cu_2SnS_3+ZnS$   | 0.08       | <sup>32</sup> |                                 | $Cu_2SnS_3+MgS$   | -0.01      |      |
| <b><math>Cu_2CdSnS_4</math></b> | $Cu_2S+CdS+SnS_2$ | 0.51       | <sup>29</sup> | <b><math>Cu_2CaSnS_4</math></b> | $Cu_2S+CaS+SnS_2$ | -0.23      | -    |
|                                 | $2CuS+CdS+SnS$    | 0.35       | <sup>30</sup> |                                 | $2CuS+CaS+SnS$    | -0.39      |      |
|                                 | $Cu_2SnS_3+CdS$   | 0.03       | <sup>38</sup> |                                 | $Cu_2SnS_3+CaS$   | -0.71      |      |
| <b><math>Cu_2HgSnS_4</math></b> | $Cu_2S+HgS+SnS_2$ | 0.56       | <sup>35</sup> | <b><math>Cu_2SrSnS_4</math></b> | $Cu_2S+SrS+SnS_2$ | -0.35      | -    |
|                                 | $2CuS+HgS+SnS$    | 0.37       | <sup>36</sup> |                                 | $2CuS+SrS+SnS$    | -0.51      |      |
|                                 | $Cu_2SnS_3+HgS$   | 0.08       |               |                                 | $Cu_2SnS_3+SrS$   | -0.83      |      |
|                                 |                   |            |               | <b><math>Cu_2BaSnS_4</math></b> | $Cu_2S+BaS+SnS_2$ | -0.48      | -    |
|                                 |                   |            |               |                                 | $2CuS+BaS+SnS$    | -0.64      |      |
|                                 |                   |            |               |                                 | $Cu_2SnS_3+BaS$   | -0.97      |      |

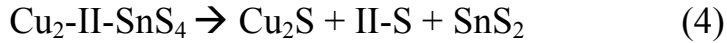
In contrast to  $I_2-II-IV-VI_4$  with  $II=Zn, Cd, Hg$ , those with  $II= Mg, Ca, Sr, Ba$  do not have a stable region in the chemical potential space, indicating that they cannot be synthesized and stable from a thermodynamic perspective. For example,  $Cu_2MgSnS_4$  does not have a stable (black) region in the  $\mu_{Cu}=-0.2$  eV plane (see Fig. 3(b)), as well as in other planes with different  $\mu_{Cu}$  which are not shown here. The main reason for the disappearing of the stable region is from the constraint of MgS and  $Cu_2SnS_3$ , i.e., the MgS line is on the left side of the  $Cu_2SnS_3$  line in Fig. 3(b). This constraint can be described by the following phase-separation reaction,



The calculated energy change of this reaction is exothermic ( $\Delta E < 0$  in Table I), meaning that the phase separation of  $Cu_2MgSnS_4$  will proceed spontaneously, in accordance with the disappearance of the stable region in the chemical potential space. Similarly, for  $Cu_2CaSnS_4$ ,  $Cu_2SrSnS_4$ ,  $Cu_2BaSnS_4$ , they do not form stable regions either, and their phase-separation reactions corresponding to Eq. (3) are exothermic.



Furthermore, these three compounds also have other phase-separation pathways,



which are also exothermic (Table I) and can proceed spontaneously. Our analysis showing that the instability for these compounds are directly related to the fact that for group IIA elements they are more stable in the ionic rocksalt structure with S than in the more covalent tetrahedral environment as in kesterite. The instability increases ( $\Delta E$  becomes more negative) when the ionicity increases as the II changes from Mg to Ca to Sr to Ba. According to the calculated results, we predict that  $\text{I}_2\text{-II-IV-VI}_4$  with II=Mg, Ca, Sr, Ba are not thermodynamically stable, and their synthesis and application in real devices are questionable. However, we noticed that there are several experimental reports about the synthesis of  $\text{Cu}_2\text{MgGeS}_4$ <sup>17</sup>,  $\text{Cu}_2\text{SrSnS}_4$  and  $\text{Cu}_2\text{CaSnS}_4$ <sup>20</sup>. We suggest that these samples are only metastable and secondary phases may exist in these samples. More experimental study on these samples is needed.

### 3.2.2. Stability of $\text{Cu}_2\text{Zn-IV-S}_4$ (IV=Si, Ge, Sn, Pb, and Ti, Zr, Hf)

Besides the substitution of the group II elements, the substitution of the group IV elements also leads to a series of  $\text{I}_2\text{-II-IV-VI}_4$  semiconductors. Here we take  $\text{Cu}_2\text{Zn-IV-S}_4$  with IV=Si, Ge, Sn, Pb, and Ti, Zr, Hf as examples, to see whether these element substitutions are limited by the thermodynamic stability.

Table II lists the calculated energy change for the possible phase-separation reactions of these compounds. Obviously,  $\text{Cu}_2\text{ZnSiS}_4$ ,  $\text{Cu}_2\text{ZnGeS}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  are stable against all the studied phase-separation pathways, consistent with the wide report of their synthesis. However, when IV=Pb, Ti, Zr, Hf all the  $\text{Cu}_2\text{Zn-IV-S}_4$  compounds prefer phase-separation to binary or ternary compounds, because at least one of their phase-separation reactions have negative energy change. This indicates that the chemical binding in the binary and ternary compounds is stronger (thus lower formation energy) than in the quaternary ones. Two trends can be found in the energy change  $\Delta E$ : (i) for the reaction corresponding to Eq. (5),  $\text{Cu}_2\text{Zn-IV-S}_4 \rightarrow 2\text{CuS} + \text{ZnS} + \text{IV-S}$ ,  $\Delta E$  decreases from Si to Ge to Sn, and turning to be negative for IV=Pb. This is because for the heavy element Pb, due to relativistic effects, it prefers to be in the 2+ ionization state as in the rocksalt PbS instead to be in the 4+ ionization state as in the tetrahedral environment associated with kesterite structure; (ii) for the reaction corresponding to Eq. (4),  $\text{Cu}_2\text{Zn-IV-S}_4 \rightarrow \text{Cu}_2\text{S} + \text{ZnS} + \text{IV-S}_2$ ,  $\Delta E$  decreases from positive to negative as IV changes from Ti to Zr to Hf, indicating that for Hf with more delocalized 5d valence orbital, it prefers to form more ionic binary  $\text{HfS}_2$  structure rather than the tetragonal Hf-S bond in quaternary  $\text{Cu}_2\text{ZnHfS}_4$ . (iii) for  $\text{Cu}_2\text{Zn-IV-S}_4 \rightarrow \text{Cu}_2\text{-IV-S}_4 + \text{ZnS}$ , the stability of  $\text{Cu}_2\text{Zn-IV-S}_4$  increases slightly when group IV elements change from Ti to Zr to Hf due to increased strain relaxation in the quaternary compounds than in the ternary  $\text{Cu}_2\text{-IV-S}_3$  when the size of group IV

elements increases. Considering these trends, we predict that it should be more difficult to form I<sub>2</sub>-II-IV-VI<sub>4</sub> compounds when group IV elements become heavy due to the separation to the binary and ternary competing compounds.

TABLE II: The calculated energy change  $\Delta E$  (in eV) of Cu<sub>2</sub>Zn-IV-VI<sub>4</sub> (IV=Si, Ge, Sn, Pb, and Ti, Zr, Hf, VI=O, S, Se, Te), through different phase-separation reactions. If the compound has been synthesized, the references are listed in the Ref. column. Because SiS, PbS<sub>2</sub>, SnTe<sub>2</sub>, Cu<sub>2</sub>TiS<sub>3</sub>, Cu<sub>2</sub>ZrS<sub>3</sub>, Cu<sub>2</sub>HfS<sub>3</sub> and Cu<sub>2</sub>SnO<sub>3</sub> have not yet been synthesized or their structures have not been reported, we assume that they take the corresponding structures of SnS, SnS<sub>2</sub> and Cu<sub>2</sub>SnS<sub>3</sub> when calculating  $\Delta E$  of the possible phase-separation reactions.

| Compound                                | Phase Separation                          | $\Delta E$ | Ref.          | Compound                                | Phase Separation                          | $\Delta E$ | Ref.          |
|---|---|------------|---------------|---|---|------------|---------------|
| <b>Cu<sub>2</sub>ZnSiS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+SiS <sub>2</sub>    | 0.48       | <sup>39</sup> | <b>Cu<sub>2</sub>ZnTiS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+TiS <sub>2</sub>    | 0.15       | -             |
|   | 2CuS+ZnS+SiS                              | 1.89       | <sup>40</sup> |   | 2CuS+ZnS+TiS                              | 1.14       |               |
|   | Cu <sub>2</sub> SiS <sub>3</sub> +ZnS     | 0.16       |               |   | Cu <sub>2</sub> TiS <sub>3</sub> +ZnS     | -0.05      |               |
| <b>Cu<sub>2</sub>ZnGeS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+GeS <sub>2</sub>    | 0.73       | <sup>6</sup>  | <b>Cu<sub>2</sub>ZnZrS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+ZrS <sub>2</sub>    | -0.27      | -             |
|   | 2CuS+ZnS+GeS                              | 0.79       | <sup>41</sup> |   | 2CuS+ZnS+ZrS                              | 1.20       |               |
|   | Cu <sub>2</sub> GeS <sub>3</sub> +ZnS     | 0.08       |               |   | Cu <sub>2</sub> ZrS <sub>3</sub> +ZnS     | -0.03      |               |
| <b>Cu<sub>2</sub>ZnSnS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+SnS <sub>2</sub>    | 0.56       | <sup>37</sup> | <b>Cu<sub>2</sub>ZnHfS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+HfS <sub>2</sub>    | -0.40      | -             |
|   | 2CuS+ZnS+SnS                              | 0.40       | <sup>33</sup> |   | 2CuS+ZnS+HfS                              | 1.73       |               |
|   | Cu <sub>2</sub> SnS <sub>3</sub> +ZnS     | 0.08       | <sup>32</sup> |   | Cu <sub>2</sub> HfS <sub>3</sub> +ZnS     | 0.04       |               |
| <b>Cu<sub>2</sub>ZnPbS<sub>4</sub></b>  | Cu <sub>2</sub> S+ZnS+PbS <sub>2</sub>    | 1.00       | -             | <b>Cu<sub>2</sub>ZnSnO<sub>4</sub></b>  | Cu <sub>2</sub> O+ZnO+SnO <sub>2</sub>    | -1.71      |               |
|   | 2CuS+ZnS+PbS                              | -0.60      |               |   | 2CuO+ZnO+SnO                              | -0.38      |               |
|   | Cu <sub>2</sub> PbS <sub>3</sub> +ZnS     | -0.11      |               |   | Cu <sub>2</sub> SnO <sub>3</sub> +ZnO     | -0.07      |               |
| <b>Cu<sub>2</sub>ZnSnSe<sub>4</sub></b> | Cu <sub>2</sub> Se+ZnSe+SnSe <sub>2</sub> | 0.76       | <sup>42</sup> | <b>Cu<sub>2</sub>ZnSnTe<sub>4</sub></b> | Cu <sub>2</sub> Te+ZnTe+SnTe <sub>2</sub> | 0.78       | <sup>43</sup> |
|   | 2CuSe+ZnSe+SnSe                           | 0.38       | <sup>37</sup> |   | 2CuTe+ZnTe+SnTe                           | 0.08       |               |
|   | Cu <sub>2</sub> SnSe <sub>3</sub> +ZnSe   | 0.05       |               |   | Cu <sub>2</sub> SnTe <sub>3</sub> +ZnTe   | 0.03       |               |

The above discussed instability is reflected by the absence of favorable regions in chemical potential space for the formation of Cu<sub>2</sub>Zn-IV-S<sub>4</sub> with IV=Pb, Ti, Zr, Hf. In Fig. 3(c), the limits are plotted for Cu<sub>2</sub>ZnTiS<sub>4</sub>, where no stable (black) region exists, because of the relative stability of Cu<sub>2</sub>TiS<sub>3</sub>. Experimentally Cu<sub>2</sub>TiS<sub>3</sub> has not yet been synthesized, and appears to be unstable with respect to further phase-separation into Cu<sub>4</sub>TiS<sub>4</sub> and TiS<sub>2</sub>,<sup>44</sup> indicating that the energy change of the phase-separation reaction  $2\text{Cu}_2\text{ZnTiS}_4 \rightarrow 2\text{ZnS} + \text{Cu}_4\text{TiS}_4 + \text{TiS}_2$  can have even larger value (more negative). Recently Cu<sub>2</sub>ZnTiS<sub>4</sub> (Cu<sub>2</sub>ZnTiSe<sub>4</sub>) had been designed and proposed as candidate solar

cell absorber materials for their band gaps comparable with  $\text{Cu}_2\text{ZnSnS}_4$  ( $\text{Cu}_2\text{ZnSnSe}_4$ ) and higher absorption coefficient<sup>18</sup>. However, the present calculation of their thermodynamic stability shows that the two quaternary compounds with Ti are only metastable, which is a serious challenge to their real application besides other issue related to this compound such as poor transport property.<sup>45</sup>

### 3.2.3. Stability of $\text{Cu}_2\text{Zn-Sn-VI}_4$ (VI=O, S, Se, Te)

In Table II, we also listed the phase-separation energy change of  $\text{Cu}_2\text{ZnSn-VI}_4$  with VI=O, S, Se, Te. We find that when VI = O, the  $\text{Cu}_2\text{ZnSnO}_4$  compound is not stable. The phase-separations into  $\text{Cu}_2\text{O}+\text{ZnO}+\text{SnO}_2$  and  $2\text{CuO}+\text{ZnO}+\text{SnO}$  are both exothermic, which means that the bonding in some of the binary oxides is much stronger than in the quaternary  $\text{Cu}_2\text{ZnSnO}_4$ . Indeed, when bound to oxygen,  $\text{Cu}^{\text{I}}$  tends to favor linear coordination environments as demonstrated in  $\text{Cu}_2\text{O}$  and related delafossite ternary oxides and  $\text{SnO}_2$  like to form the rutile structure. In Fig. 3(d), the chemical potential limit is plotted for  $\text{Cu}_2\text{ZnSnO}_4$ , in which the strong stability of  $\text{SnO}_2$  makes the stable region disappear. Considering the large negative energy-change of the phase-separation reactions and the strong constraint to the chemical potential range, the synthesis of single-phase  $\text{Cu}_2\text{ZnSnO}_4$  would be challenging.

Recently, Washio *et al.* and Yang *et al.* both reported synthesis of the mixed-anion  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{O}_x)_4$  alloys with the O composition (x) as high as 60% and 27% respectively<sup>19, 46</sup>. They stated that “Oxygen is another group VI element and can replace S in CZTS without disturbing valence. Therefore,  $\text{Cu}_2\text{ZnSnS}_{4-x}\text{O}_x$  (CZTSO) can also be suitable for thin film solar cells.” However, our calculations show that  $\text{Cu}_2\text{ZnSnO}_4$  compound is unstable due to the preference of oxides to have different structure and coordination, thus makes this suggestion questionable. Since  $\text{Cu}_2\text{ZnSnS}_4$  is stable, while  $\text{Cu}_2\text{ZnSnO}_4$  is unstable with respect to phase separation, there should exist a critical value for the O composition, below which  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{O}_x)_4$  alloys isostructural to  $\text{Cu}_2\text{ZnSnS}_4$  can be stabilized. When the O composition is higher than the critical value,  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{O}_x)_4$  alloys will be unstable, and the coexistence of secondary compounds – particularly binary metal oxides – are likely to form in the synthesized samples. Based on this, it is necessary to investigate the phase separation in the synthesized samples of these alloys, especially when O composition is high. In contrast to  $\text{Cu}_2\text{ZnSn}(\text{S},\text{O})_4$ , the alloys formed by mixing  $\text{Cu}_2\text{ZnSnS}_4$ ,  $\text{Cu}_2\text{ZnSnSe}_4$ , and  $\text{Cu}_2\text{ZnSnTe}_4$  are stable, e.g., the  $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$  alloys have been synthesized with the composition parameter x tunable from 0 to 1<sup>47, 48</sup>, so the properties can be tuned continuously in a wide composition range.

## IV. CONCLUSIONS

Using the first-principles calculations, we have studied the thermodynamic stability of three classes of tetrahedral  $\text{I}_2\text{-II-IV-VI}_4$  compound semiconductors. We show that

only those with II=Zn, Cd, Hg, IV=Si, Ge, Sn and VI=S, Se, Te are stable, but those with II=Mg, Ca, Sr, Ba, IV=Ti, Zr, Hf, and VI=O are unstable because of the phase-separation into the competing binary and ternary compounds. We find that for those unstable compounds, the materials are more ionic and their binary and ternary secondary phases tend to form non-tetrahedral structures such as six-fold rock salt structure. As a result of the limited stability, these elements can only be alloyed into the stable  $I_2-II-IV-VI_4$  semiconductors with a low composition, and thus their contribution to tuning the material properties such as band gaps is limited. Some unstable  $I_2-II-IV-VI_4$  compounds have been reportedly synthesized, including  $Cu_2SrSnS_4$ ,  $Cu_2BaSnS_4$ ,  $Cu_2MgGeS_4$  and  $Cu_2ZnSn(S_{1-x}O_x)_4$  alloys with a high O composition. We suggest that further study is needed, especially the detection of the secondary compounds in the synthesized samples, which could have similar X-Ray diffraction patterns.<sup>49</sup> Our results could provide guideline of understanding the thermodynamic stability limit in the design of new quaternary semiconductors.

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